

## Catalytic hydrogen currents at DME in the presence of thio compounds

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**Abstract.** Polarographic catalytic hydrogen currents were studied in ammonium chloride – ammonium hydroxide buffered solutions of various thio compounds in the presence of chromium (VI) ion. It was found that the catalytic activities of structurally similar thio compounds decrease in the following order: pentamethylene dithiocarbamate > diethyl dithiocarbamate > ammonium pyrrolidine dithiocarbamate > potassium ethyl xanthate

**Keywords.** Dithiocarbamates; catalytic hydrogen currents; chromium (VI).

### 1. Introduction

A survey of literature shows that the catalytic activity of structurally similar thio compounds decreases with the decreasing values of the stability constants of their complexes, which is directly related with the dissociation constants of the ligands (Brezina and Gultjaj 1963; Kadlecek *et al* 1978). The same order was observed in our study with the thio compounds based on their dissociation constants.

The catalytic effect of chromium with a few thio compounds has been reported earlier from these laboratories (Saraswathi *et al* 1990) and the method developed was applied only to the analysis of trace levels of chromium(VI) and (III) in drinking water, industrial effluents, agricultural materials, ore and stainless steel samples.

In the present study, the results of the dissociation constants of potassium ethyl xanthate (Xanthate), ammonium pyrrolidine dithiocarbamate (Apdte), diethyl dithiocarbamate (Dedte) and sodium pentamethylene dithiocarbamate (Pipdte) and their direct correlation with the sensitivity of catalytic activity of Cr(VI) are presented.

### 2. Experimental

The ligands sodium pentamethylene dithiocarbamate and potassium ethyl xanthate were prepared by well-established methods (Glue and Schwab 1950; Vogel 1988). Ammonium pyrrolidine dithiocarbamate (Apdte) and Diethyl dithiocarbamate (Dedte) have been procured from Sd Fine Chemicals Pvt. Ltd., Bombay and Loba Chemie Indo Australan Co., Bombay, respectively. Potassium chromate, ammonium chloride and ammonium hydroxide were of analytical reagent grade. Solutions were prepared in double distilled water.

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All the measurements were carried out in a pure nitrogen atmosphere at a temperature of  $25^\circ \pm 1^\circ\text{C}$ . Dropping mercury electrode (DME) with a drop time of 3.8 s with an LR-101 D.C. Recording Polarograph and LI-10 pH meter (both from Elico Pvt. Ltd., India) were used.

### 3. Results and discussion

The catalytic polarographic curves of the four thio compounds in the presence of Cr(VI) are shown in figure 1. To compare the ability of different thio compounds to catalyze the hydrogen evolution, the value of the Brdicka current,  $I_B$ , was measured at a thio compound concentration of 0.4 mM. Catalytic activity is found to decrease (table 1) in the order, Pipdtc > Dedtc > Apdtc > Xanthate. The same sequence was seen by plotting a graph between catalyst concentration ( $C_{\text{cat}}$ ) and the height of the catalytic waves (figure 2). It was found that with increasing  $C_{\text{cat}}$  the limiting catalytic current increases, at first linearly with  $C_{\text{cat}}$ . The increase of the wave height then becomes slower. Finally, at high  $C_{\text{cat}}$  values, the limiting catalytic current becomes independent of  $C_{\text{cat}}$  and reaches a certain limit (Mader *et al* 1982). A similar relation was observed with all the four thio compounds studied.

The order of catalytic activity of thio compounds is further confirmed with the

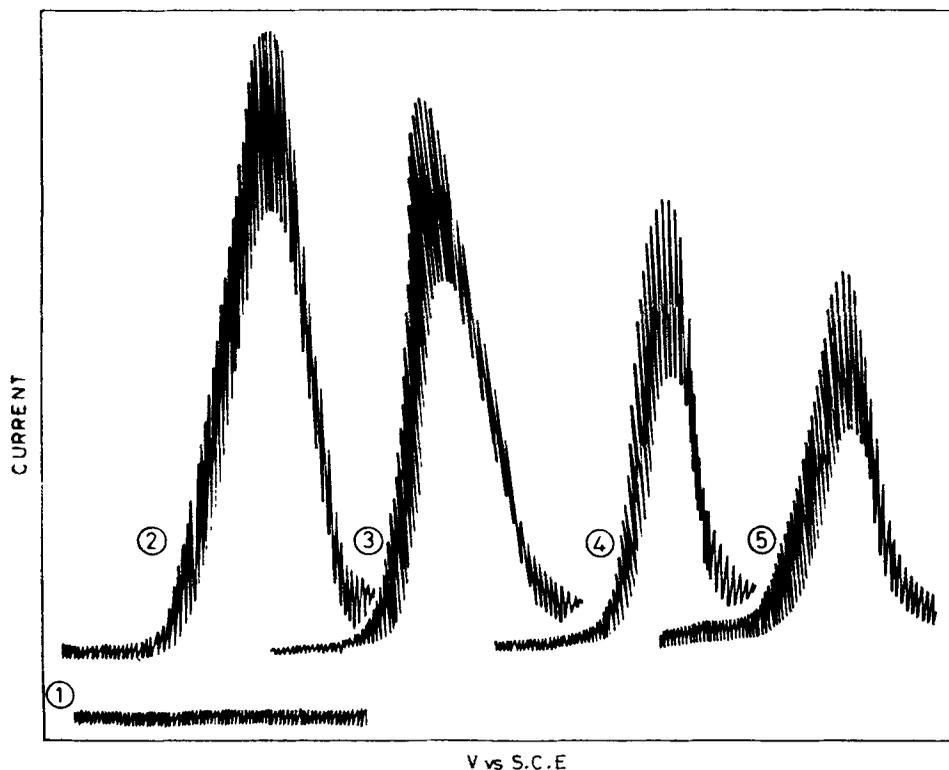
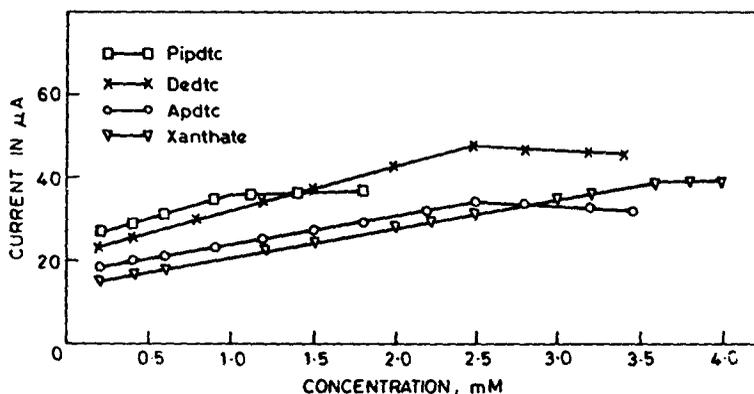


Figure 1. Polarographic curves of (1)  $\text{NH}_4\text{Cl}$  (0.4 M) + Cr (VI) (0.1 mM) pH  $\sim$  8.2 with: (2) Pipdtc; (3) Dedtc; (4) Apdtc; (5) Xanthate (concentration 0.4 mM), starting potential  $-1.2$  V.

**Table 1.** Catalytic activity of some dithio carbamates.

Dithio carbamates	Catalytic activity ( $\mu\text{A}$ )	$-\log K_L$
Pipdte	29.0	9.5
Dedtc	25.0	9.0
Apdte	20.5	7.5
Xanthate	17.0	7.5

**Figure 2.** The dependence of the catalytic current on the concentration of this compounds.

ligand dissociation constants ( $-\log K_L$ ) obtained pH-metrically and their values are 9.5, 9.0, 7.5 and 7.5 for Pipdte, Dedtc, Apdte and Xanthate respectively.

The catalytic nature of the wave may be due to the evolution of hydrogen as expected with thio compounds. The complexes of transition metal ions with thio compounds are found to accelerate the catalytic activity of organic compounds containing  $-\text{SH}$  groups due to the high adsorptivity (Mairanovskii 1963; Mader *et al* 1982).

The foregoing discussion indicates that the catalytic activities of the structurally similar thio compounds decrease with decreasing values of the dissociation constants of the ligands.

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